Diesters of Lactic Acid. Adipates of Various Lactates[1,2]

By C. E. Rehberg and Marion B. Dixon

The hydroxyl group in esters of lactic acid may be readily esterified by use of carboxylic acids, anhydrides or acyl chlorides. Previous papers from this laboratory have described the acetates,[3] laurates,[4] acrylates,[5] alkyl carbonates[6] and diethylene glycol bis-carbonates[7] of various lactates.

Adipic acid was of special interest in this work because of its availability at low cost and the potential utility of its lactate esters as plasticizers.

The lactate adipates studied (Table I) have the type formula

$$\begin{array}{l} COOCH(CH_3)COOR \\ | \\ (CH_2)_4 \\ | \\ COOCH(CH_3)COOR \end{array}$$

where R is the radical of the alcohol from which the lactate was made. These esters were conveniently made from adipyl chloride and the lactates. Less pure products but equally good plasticizers can be made by the direct esterification of adipic acid with the lactic ester.[8]

All of the esters were clear, colorless, oily liquids having little or no odor. Data on their use as plasticizers will be published elsewhere.

Boiling Points.—Each ester was distilled, and constant boiling fractions were used for the determination of boiling points and other physical properties. Figures 1 and 2 were drawn from boiling points determined with a recently described alembic type tensimeter-still.[9] The temperature coördinates of these figures (Cox charts) were laid off as linear functions of $1/(t° + 223)$. This was easily achieved[10] by adding 50° to each calibration mark on a Cox chart graduated according to $1/(t° + 273)$.

Boiling points of the esters at 1 mm. pressure were taken from Figs. 1 and 2 and plotted *vs.* the normal boiling points of the alcohols ROH. These points fell approximately on a straight line, the equation of which was $B_E = 0.67\ B_A + 115$, where B_E = b. p. of the ester at 1 mm. and B_A = b. p. of ROH

Table I

Adipates of Lactic Esters $[—CH_2CH_2COOCH(CH_3)COOR]_2$

	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sapn. equiv. Calcd.	Sapn. equiv. Found	n^{20}_D	n^{40}_D	d^{20}_4	d^{40}_4	Viscosity, cps. 20°	Viscosity, cps. 40°	Mol refract. Calcd.	Mol refract. Found 20°
Ethyl	91	55.5	55.2	7.6	7.6	86.6	86.1	1.4412	1.4340	1.1075	1.0883	49.56	18.83	82.70	82.60
Propyl	62	57.7	57.5	8.1	8.3	93.6	91.1	1.4432	1.4370	1.0865	1.0681	61.53	24.26	91.94	91.38
Butyl	96	59.7	59.9	8.5	8.8	100.6	99.7	1.4432	1.4360	1.0543	1.0365	41.37	16.56	101.18	101.24
Isobutyl	98	59.7	59.8	8.5	8.4	100.6	99.6	1.4410	1.4340	1.0479	1.0299	53.29	20.13	101.18	101.44
s-Butyl	88	59.7	59.5	8.5	8.9	100.6	98.6	1.4410	1.4338	1.0574	1.0394	75.58	27.06	101.18	100.52
2-Ethylhexyl	96	65.3	65.2	9.8	9.8	128.7	128.4	1.4494	1.4420	0.9997	0.9836	67.97	25.63	138.12	138.17
n-Octyl	93	65.3	65.2	9.8	9.6	128.7	127.7	1.4482	1.4414	.9960	.9801	53.71	22.47	138.12	138.37
2-Octyl	85	65.3	65.2	9.8	9.9	128.7	125.6	1.4446	1.4375	.9929	.9769	82.4	23.55	138.12	137.83
3,5,5-Trimethylhexyl	87	66.4	66.3	10.0	10.0	135.7	134.7	1.4500	1.4430	.9881	.9733	117.0	37.75	147.36	147.61
Allyl[a]	85	58.4	58.2	7.1	7.1	92.6	91.8	1.4565	1.4485	1.1085	1.0892	41.98	16.39	91.01	90.92
2-Butoxyethyl	62	58.8	58.7	8.6	8.6	122.6	120.2	1.4472	1.4401	1.0668	1.0508	71.93	26.10	122.93	122.02
2-Hexyloxyethyl	90	61.5	61.3	9.2	9.0	136.7	137.8	1.4490	1.4419	1.0327	1.0161	66.54	24.96	141.41	141.98
2-(2-Butoxyethoxy)-ethyl	60	58.1	58.2	8.7	8.8	144.7	146.0	1.4507	1.4433	1.0725	1.0559	79.19	31.42	144.69	145.19
Tetrahydrofurfuryl	78	57.6	57.1	7.5	7.7	114.6	112.6	1.4680	1.4610	1.1677	1.1516	525.9	123.5	109.30	109.15
1-Carbethoxyethyl[b]	87	53.9	53.9	7.0	6.8	81.8	81.8	1.4462	1.4390	1.1478	1.1285	543.5	95.0	113.72	114.01
1-Carbobutoxyethyl[c]	98	57.1	57.0	7.7	7.7	91.1	91.9	1.4470	1.4400	1.1026	1.0842	283.5	67.9	132.19	132.42

[a] This ester has been reported by Howald and Jones, U. S. Patent 2,462,042, February 15, 1949. Their physical constants are in substantial agreement with ours. [b] Adipate of ethyl acetyllactate. [c] Adipate of butyl lactyllactate.

Table II

Preparation and Properties of Lactic Esters

Lactate	Yield, %	Boiling point °C.	Boiling point Mm.	n^{20}_D	d^{20}_4	Mol. refraction Calcd.	Mol. refraction Found	Sapn. equiv. Calcd.	Sapn. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-Octyl	83	54	0.2	1.4300	0.9300	56.18	56.18	202.3	198.0	65.3	65.4	11.0	11.2
3,5,5-Trimethylhexyl	86	80	.3	1.4365	.9236	60.80	61.29	216.3	220.5	66.6	66.6	11.2	11.2
2-Hexyloxyethyl	83	82	.3	1.4362	.9829	57.82	58.09	218.3	223.3	60.5	60.9	10.2	10.6
1-Carbethoxyethyl[a]	25[b]	77	1.0	1.4292	1.1136	43.98	44.05	95.1	94.8	50.5	50.4	7.4	7.5
1-Carbobutoxyethyl[c]	22[b]	94	1.0	1.4329	1.0622	53.21	53.38	109.1	108.8				

[a] Ethyl lactyllactate. [b] Conversion of lactate to lactyllactate. [c] Butyl lactyllactate.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

(2) Presented in part before the Division of Paint, Varnish and Plastics Chemistry, American Chemical Society, Chicago, Ill., April 1948 and Detroit, Mich., April 1950. Article not copyrighted.

(3) Rehberg and Dixon, This Journal, **72**, 1918 (1950).

(4) Fein and Fisher, *J. Org. Chem.*, **15**, 530 (1950).

(5) Rehberg, Dixon and Fisher, This Journal, **67**, 208 (1945).

(6) (a) Rehberg, Dixon and Fisher, *J. Org. Chem.*, **13**, 254 (1948); (b) Rehberg and Dixon, *ibid.*, **15**, 565 (1950).

(7) (a) Rehberg, Dixon and Fisher, *ibid.*, **14**, 593 (1949); **15**, 560 (1950); (b) *Ind. Eng. Chem.*, **42**, 1409 (1950).

(8) Rehberg and Dixon, "Plasticizers from Lactic Acid. Direct Esterification of Butyl Lactate with Adipic Acid," presented before the Division of Paint, Varnish and Plastics Chemistry, American Chemical Society, Atlantic City, N. J., September 1949.

(9) Ratchford and Rehberg, *Anal. Chem.*, **21**, 1417 (1949).

(10) Rehberg, *Ind. Eng. Chem.*, **42**, 829 (1950).

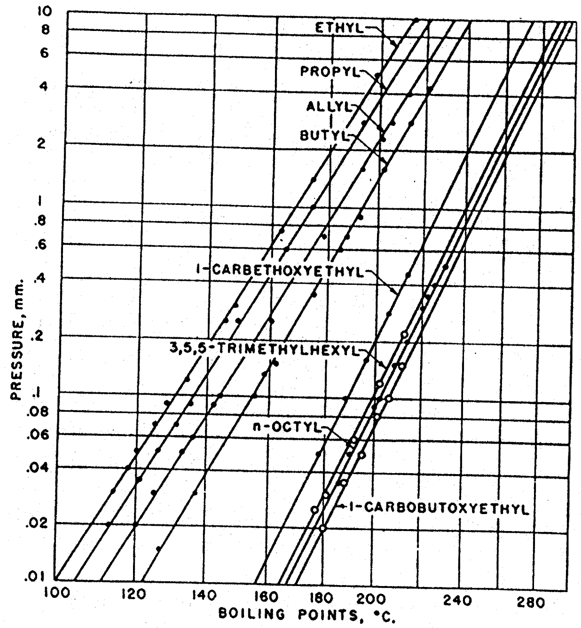

Fig. 1.—Boiling points of lactate adipates.

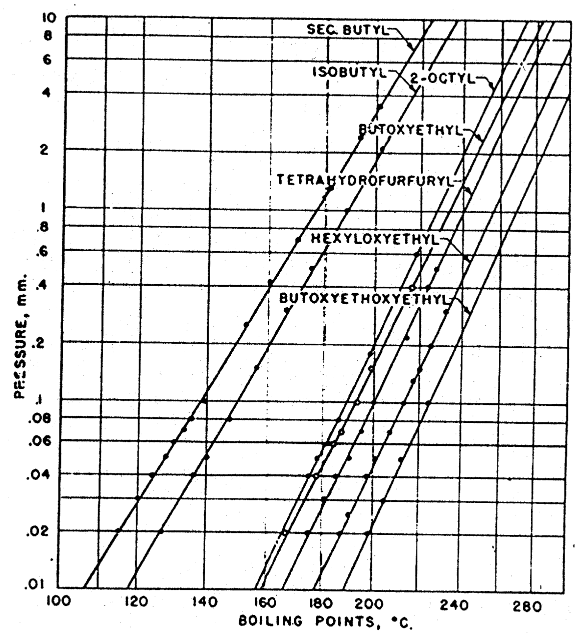

Fig. 2.—Boiling points of lactate adipates.

at atmospheric pressure. The maximum deviation from this line was 8° and the average was 4°. This equation is convenient for the estimation of the boiling points of lactate adipates for which data are not available.

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Experimental

Lactates.—Ethyl and butyl lactates are available commercially. All the others except those in Table II have been reported previously[11] and were prepared by direct esterification[11d] of lactic acid or by the alcoholysis[6a] of methyl or ethyl lactate.

Ethyl and butyl lactyllactates (Table II) have been reported by Claborn[12] who made them by the reaction of lactide with the appropriate alcohol. We prepared these esters by the self-alcoholysis[13] of the corresponding lactate. Briefly, the lactate, containing about 0.2% of sulfuric acid, was refluxed in a still while approximately the theoretical amount of alcohol was distilled out. The catalyst was then neutralized, and the product was distilled at the lowest practicable temperature.

Reaction of Adipyl Chloride with Lactates.—One mole of lactate and one mole of pyridine were dissolved in 200 to 300 cc. of anhydrous ether. This solution was stirred and maintained at 0–10°, while one-half mole of adipyl chloride was added dropwise. After being left for several hours at room temperature, the reaction mixture was washed with water, dried and distilled. For the distillation, a short Vigreux column or an alembic type still[9] was most suitable. The latter was used exclusively for determination of boiling points.

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(11) (a) Smith and Claborn, *ibid.*, **32**, 692 (1940); (b) Fein, Ratchford and Fisher, This Journal, **66**, 1201 (1944); (c) Fein and Fisher, *ibid.*, **68**, 2631 (1946); (d) Rehberg, *Org. Syntheses*, **26**, 4 (1946).

(12) Claborn, U. S. Patent 2,350,388, June 6, 1944.

(13) Filachione, Costello and Fisher, "Plasticizers from Lactic Acid. Esters of Polymeric Lactic Acid," presented before the Division of Paint, Varnish and Plastics Chemistry, American Chemical Society, 112th Meeting, New York, Sept. 1947.